New method for determination of heats of thermal gas-phase reactions yielding intermediates

N. N. Buravtsev, Yu. A. Kolbanovskii,* and A. A. Ovsyannikov

A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,
29 Leninsky prosp., 117912 Moscow, Russian Federation.
Fax: +7 (095) 230 2224

A new procedure for the determination of the heats of thermal gas-phase reversible reactions leading to intermediates in the framework of the adiabatic compression method is proposed. A model problem is solved, and the error of the method is evaluated (~1 %). The validity of the method was confirmed using the reversible formation of the 1,2-biradical from tetrafluoroethylene as an example.

Key words: pyrolysis, intermediates; enthalpies of reactions.

In recent years it was found that many chemical reactions involve formation of short-lived intermediates, *viz.*, carbenes and biradicals, whose existence was confirmed by the corresponding spectral data.[1,2] Due to the short lifetimes of these intermediates, direct and sufficiently reliable determination of thermal effects of their formation is still a challenging problem. This complicates the choice of the most probable mechanism, among the several mechanisms possible for each reaction.[3]

Recently a number of important results were obtained by combining the method of adiabatic compression and kinetic spectroscopy. For example, 1,2-biradicals[4,5] isomeric to lower C_2—C_4 perfluoroolefins were detected for the first time under conditilons of strictly gas-phase pyrolysis. Before these studies, the existence of 1,2-biradicals had only been suggested from general considerations.[1] Besides, the formation of the CF_3CF carbene[6] during thermal decomposition of $C_2F_5SiF_3$ and the formation of the CF_3CH carbene[7] during α,α-dehydrohalogenation of CF_3CH_2Cl were detected for the first time in the gas phase by spectroscopy.

The concept of a biradical structure of intermediates is often used in the literature dealing with mechanisms of thermal reactions, but some points remain controversial. For example, in a recent paper[3] dealing with the mechanism of isomerization of cyclopropane, it has been noted that the difficulties in the interpretation of reaction pathways are associated with the absence of reliable data on the heats of formation of intermediates and enthalpies of elementary reactions.

The purpose of the present work is to describe a method for determining the heats of the reversible reactions yielding intermediates, based on the experimental data obtained on adiabatic compression setups using kinetic spectroscopy.

Physicochemical grounds of the method

By kinetic spectroscopy using loose-piston adiabatic compression setups experimental data were obtained on the time dependences of light absorption and pressure of the reacting mixture. An example of a typical PC recording of these values is presented in Fig. 1. In addition, according to published data,[8] the maximum magnitude of the geometric degree of compression $\varepsilon_{max} = V_0/V_{min}$ is also measured (V_0 and V_{min} are the volumes of the gas prior to compression and at the instant the piston stops, respectively), which is achieved when the piston stops at the point $t = 0$ (see Fig. 1).*

For determining the enthalpy of formation of an intermediate according to the method suggested below, two conditions are to be fulfilled.

1. Since the adiabatic compression method is not isothermal to attain an equilibrium in a chemical reaction, it is necessary that the characteristic time of the temperature variation (τ_T) should be much greater than the characteristic time of the chemical reaction (τ_C):

$$\tau_T \gg \tau_C. \qquad (1)$$

According to the literature data,[9]

$$\tau_T = \frac{T}{\mathrm{d}T/\mathrm{d}t}, \qquad (2)$$

$$\tau_C = \frac{B}{\mathrm{d}B/\mathrm{d}t}, \qquad (3)$$

where B is the amount of the intermediate.

---

* $t < 0$ in Figs. 1 and 2 corresponds to compression of the mixture and $t > 0$ corresponds to its expansion.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 64—67, January, 1996.

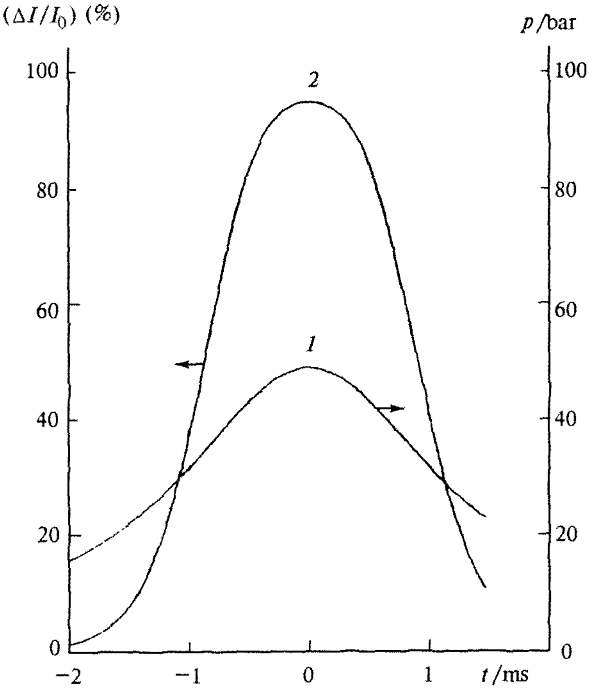

Fig. 1. Calculated curves for pressure (*1*) and light absorption (*2*) during adiabatic compression of a mixture of C_2F_4 (5 % (v/v)) with Ar (95 % (v/v)).

The temperature variation during adiabatic compression obeys the Poisson equation, and the maximum temperature of the reactants, highly diluted with an inert gas, is achieved at the instant when the compression is maximum. At this point, the dT/dt derivative is equal to zero, and dB/dt is at the maximum, and it is the point where inequality (1) is best obeyed.

2. The equilibrium in the reaction yielding the intermediate must not be disturbed by other processes involving this species. In other words, the rate of the back reaction must be appreciably greater than the overall rate of decay of the intermediate by other channels.

The conditions of the experiment are specified in such a way that the number of moles of the starting compound virtually does not change in the course of the compression—expansion cycle.

At the instant of maximum compression (t = 0), the Lambert—Beer equation for light absorption by the intermediate is written as

$$-\ln\left(1 - \frac{\Delta I(t=0)}{I_0}\right) = \sigma l B_{eq}\varepsilon_{max}/V_0, \qquad (4)$$

where $\Delta I(t = 0) = I_0 - I(t = 0)$, I_0 and I are the intensities of the incident light and the light that has passed through the studied gas, respectively; σ is the extinction coefficient; and l is the thickness of the absorbing gas layer.

The equilibrium concentration of the intermediate at this instant is found from the expression

$$B_{eq}\varepsilon_{max}/V_0 = K_{eq}(M\varepsilon_{max}/V_0) = A\exp[-\Delta Q/(RT)]M\varepsilon_{max}/V_0, \qquad (5)$$

where K_{eq} is the equilibrium constant; A is its entropy term; ΔQ is the heat of the reaction; and M is the number of moles of the starting compound.

If we express the concentration of the intermediate from Eqs. (4) and (5) and equate the resulting relationships, we obtain

$$-\frac{\Delta Q}{2.3RT(t=0)} = \log\frac{V_0\{-\ln(1-[\Delta I(t=0)/I_0])\}}{l\varepsilon_{max}M} - \log(\sigma A)\,. (6)$$

The temperature at the instant t = 0 with known pressure and volume ($V_{min} = V_0/\varepsilon_{max}$) can be calculated from the equation of state, l and V_0 are parameters of the setup, and M is determined by the initial pressure and the composition of the gas under study. The values concerning the light absorption are measured in a series of runs with various ε_{max}. Then the ΔQ value can be found by plotting the dependence of the first term (Y) of the right-hand side of Eq. (6) *vs.* $1/(RT)$ for the runs with various ε_{max}.

Test of the method with respect to a model problem

We solved the direct problem, *viz.*, a set of equations describing adiabatic compression of a gas in a loose-piston setup in the presence of chemical reactions,[8,10,11] supplemented by the Lambert—Beer equation. Parameters of the real setup, the composition of the studied gas, the initial temperature and pressure, the equilibrium constant, and the extinction coefficient of the intermediate were specified. Tetrafluoroethylene, for which the temperature dependence of the heat capacity is well known, was chosen as the model gas.[12]

The mathematical experiment yielded pressure and light absorption curves (similar to those presented in Fig. 1), whose typical example is shown in Fig. 2. The data needed for the calculation according to Eq. (6) are presented in Table 1. Their processing (Fig. 3) resulted in the expression

$$K = 10^{2.45}\exp[-21.88\ (\text{kcal mol}^{-1})/(RT)]$$

with the constant, included in the model, equal to

$$K = 10^{2.5}\exp[-22.00\ (\text{kcal mol}^{-1})/(RT)].$$

A comparison of the above-presented values shows that the error of this method is ~0.55 %, taking into account the accuracies of the calculation of model curves, the determination of the maximum pressure and compression degree, and the calculation of the heat from Eq. (6).

A different situation is observed if the errors of the measurement of the values incorporated in Eq. (6) are

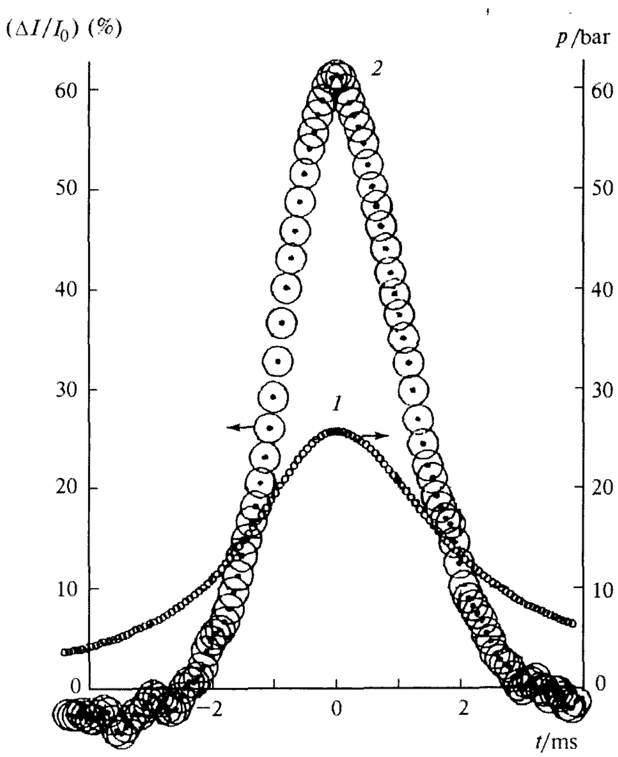

Fig. 2. Experimental curves for pressure (*1*) and light absorption (*2*) during adiabatic compression of a mixture of C_2F_4 (5 % (v/v)) with Ar (95 % (v/v)).

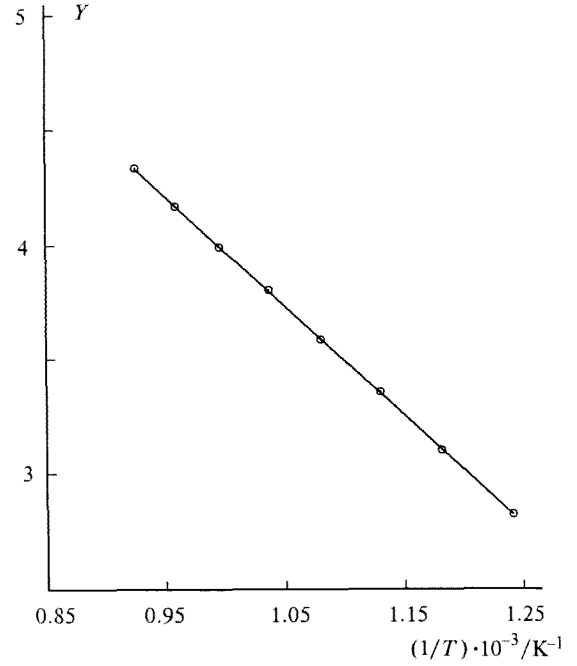

Fig. 3. Data of Table 1 (the model problem) in the coordinates of Eq. (6).

Table 1. Results of solutions of the model problem

Compression mode	p_{max} /bar	ε_{max}	$(\Delta I/I_0)_{max}$ (%)	$T_{max}\cdot10^{-3}$ /K^{-1}
1	49.22	13.45	95.25	0.93
2	43.96	12.45	85.62	0.96
3	39.07	11.50	69.60	1.00
4	34.56	10.58	50.47	1.04
5	30.40	9.70	32.73	1.08
6	26.58	8.86	19.16	1.13
7	23.00	8.06	10.21	1.19
8	19.90	7.29	4.97	1.24

taken into account. The corresponding data are present below.

Errors of the measurement of the parameters (%)	$\delta\left(\frac{\Delta I}{I_0}\right) = \pm2$	$\frac{\delta(p_{max})}{p_{max}} = \pm0.2$	$\frac{\delta(\varepsilon_{max})}{\varepsilon_{max}} = \pm0.05$
Error of the calculation ΔQ, $\delta(\Delta Q)$ /kcal mol^{-1}	$< \pm 0.1$	$< \pm 0.05$	$< \pm 0.01$

The resulting error is the sum of the errors of the measurements of the three above-mentioned parameters and amounts to ~0.1 kcal mol^{-1} or 0.5 % of a "theoretical" value of 22 kcal mol^{-1}. In view of the above-obtained value of 0.55 % caused by the errors of the calculation itself, the overall error of the method can be estimated as being 1 %.

Application of the method to a particular experiment

Figure 1 shows a typical curve of light absorption during adiabatic compression of tetrafluoroethylene diluted with argon. Previously[4] it was shown that this absorption is due to the existence of the 1,2-biradical $\dot{C}F_2\dot{C}F_2$. Similar curves were obtained with various ε_{max}. Table 2 presents the measured and calculated values included in Eq. (6), and Fig. 4 shows the results of processing the experimental data from Table 2 accord-

Table 2. Experimental and calculated values incorporated in Eq. (6)

Run	p_{max} /bar	ε_{max}	$\Delta I/I_0$ (%)	N	$T_{max}\cdot10^{-3}$ /K^{-1}
1	55.0	14.65	97.6	0.05	0.88
2	38.8	11.59	66.5	0.05	0.99
3	37.3	11.48	62.3	0.05	0.995
4	36.6	11.15	59.0	0.05	1.01
5	34.8	10.78	51.4	0.05	1.03
6	34.4	12.51	32.5	0.10	1.21

Note. N is the molar fraction of tetrafluoroethylene in its mixture with argon.

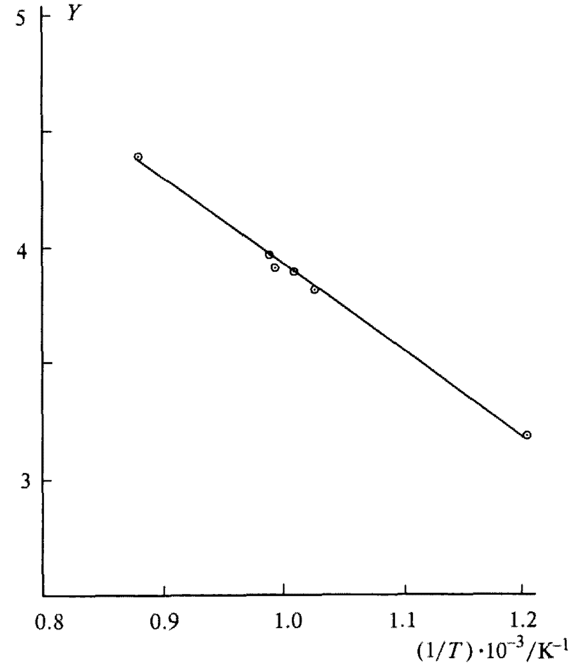

Fig. 4. Experimental data of Table 2 in the coordinates of Eq. (6).

ing to Eq. (6). The heat of the reaction thus found is 17.03±0.1 kcal mol^{-1}.

Knowing the heat of the $C_2F_4 \rightleftharpoons \dot{C}F_2\dot{C}F_2$ reaction and the tabular value for the heat of formation of C_2F_4 from the elements,[12] one can easily determine the heat of formation of the biradical, which is equal to -140 kcal mol^{-1}.

Now we present the justification of the correctness of the application of the method suggested by us to the given experiment, since the fulfillment of the second condition should be analyzed specially in each particular case.

The possible reactions of the $\dot{C}F_2\dot{C}F_2$ 1,2-biradical (apart from the back reaction, *viz.*, the formation of C_2F_4) are its addition to the double bond of the starting C_2F_4 molecule, recombination, and decomposition giving two difluorocarbenes.[4,13] The latter process does not occur under the conditions in which this series of experiments is conducted, because CF_2 is not detected by spectroscopy. According to the published data,[4] recombination processes are insignificant in the transformations of $\dot{C}F_2\dot{C}F_2$. The first of the above-listed reactions is the most important; it is this reaction that leads to the formation of octafluorocyclobutane, which is almost irreversible under the experimental conditions.

$$\dot{C}F_2\text{—}\dot{C}F_2 + CF_2{=}CF_2 \rightleftharpoons \dot{C}F_2\text{—}CF_2\text{—}CF_2\text{—}\dot{C}F_2$$

$$\dot{C}F_2\text{—}CF_2\text{—}CF_2\text{—}\dot{C}F_2 \longrightarrow cyclo\text{-}C_4F_8$$

Therefore, the yield of the latter compound characterizes the role of this channel in the overall scheme of the process.

At the lowest temperature used in this series (825 K $\leq T \leq$ 1003 K), octafluorocyclobutane is still not detected by chromatography, and at the highest temperature, its yield is no more than several percent, *i.e.*, the contribution of this channel of the reaction of the $\dot{C}F_2\dot{C}F_2$ 1,2-biradical is small.

Note that if any reaction of the $\dot{C}F_2\dot{C}F_2$ 1,2-biradical, insignificant at low temperatures, became more important at higher temperatures, it would be impossible to obtain a straight line in the coordinates shown in Fig. 4.

The foregoing served as justification for the application of the method under consideration to this particular problem.

Thus, a principally new method for determining the heats of thermal gas-phase reactions in which intermediates are formed was suggested. The error of the method is ~1 %.

The work was carried out with financial support of the Russian Foundation for Basic Research (Project No. 95-03-09700).

References

1. *Diradicals*, Ed. W. T. Borden, Wiley-Interscience, New York, 1982.
2. *Kinetics and Spectroscopy of Carbenes and Biradicals*, Ed. M. S. Platz, Plenum, New York, 1990.
3. J. A. Berson, *Science*, 1994, **266**, 1338.
4. N. N. Buravtsev, Yu. A. Kolbanovskii, and A. A. Ovsyannikov, *Mendeleev Commun.*, 1994, 48.
5. N. N. Buravtsev, Yu. A. Kolbanovskii, and A. A. Ovsyannikov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 2048 [*Russ. Chem. Bull.*, 1995, **44**, 1967 (Engl. Transl.)].
6. N. N. Buravtsev, L. S. German, A. S. Grigor'ev, Yu. A. Kolbanovskii, and A. A. Ovsyannikov, *Mendeleev Commun.*, 1993, 133.
7. N. N. Buravtsev, A. S. Grigor'ev, Yu. A. Kolbanovskii, and A. A. Ovsyannikov, *Dokl. Akad. Nauk*, 1994, **339**, 616 [*Dokl. Chem.*, 1994, **339** (Engl. Transl.)].
8. Yu. A. Kolbanovskii, V. S. Shchipachev, N. Ya. Chernyak, A. S. Chernysheva, and A. S. Grigor'ev, *Impul'snoe szhatie gazov v khimii i tekhnologii* [*Pulse Compression of Gases in Chemistry and Technology*], Nauka, Moscow, 1982 (in Russian).
9. Yu. A. Kolbanovskii, A. A. Levitskii, and L. S. Polak, *Kinet. Katal.*, 1989, **30**, 447 [*Kinet. Catal.*, 1989, **30** (Engl. Transl.)].
10. A. G. Merzhanov, *Neizotermicheskie metody v khimicheskoi kinetike* [*Nonisothermal Methods in Chemical Kinetics*], Preprint of the Institute of Chemical Physics in Chernogolovka, 1973 (in Russian).
11. Yu. A. Kolbanovskii, *Usp. Khim.*, 1989, **58**, 1800 [*Russ. Chem. Rev.*, 1989, **58** (Engl. Transl.)].
12. D. R. Stull, E. F. Westram, and G. C. Zinke, *The Chemical Thermodynamics of Organic Compounds*, J. Wiley, New York, 1969.
13. N. N. Buravtsev, L. S. German, A. S. Grigor'ev, Yu. A. Kolbanovskii, and A. A. Ovsyannikov, *Mendeleev Commun.*, 1994, 190.

Received April 25, 1995;
in revised form May 24, 1995